**2nd quantization**

Still goin…

**Perturbation Theory**

The usual RS or BW time-independent formulas for calculating eigenenergies and states holds here as well as before in other contexts. So too does the time-dependent perturbation theory. For instance, say we had a Hamiltonian,



where εi are the free particle energies, and V2 is some interaction between the particles. Then the free particle states / energies are:



where the n’s are occupation numbers. And we could apply the usual rules,



where,



to get the corrections to the free-particle states and energies (and we can evaluate that expection because we know how the creation/annihilation operators act on states). But this is usually pretty nasty (though a lot better than doing it in the Hilbert Space like we would’ve had to do before 2nd quantization), and so other methods are often sought, usually involving GF’s. But sometimes this *is* actually the best way.

**Example**

It’s worthwhile to consider how one might try to find the energy levels of a 2nd quantized H. So let’s consider some:



*One way*

is to try to find single particle eigenvectors (this way would only work if we did have single particle eigenvectors – and if we have interactions in our system, then we may not). Once we have the single particle eigenvectors/energies, then we know the multi-particle eigenvectors/energies. So let’s say,



(where |0> is the vacuum state (i.e. zero particles) which is to say it is some linear combination to-be-determined of single particle states. Plugging this in, and let’s say we’re dealing with fermions for the sake of discussion:



So the guy in parentheses must be zero, for the LHS to be zero. So we have an eigenvalue equation (basically the Schrodinger equation) for the single particle energies:



Now there will be as many solutions to this equation as is the dimensionality of the Hilbert Space. And since elementary excitations are given by:



This would mean that the creation/annihilation operators for such elementary excitations are:



Of course ψk(E) would have to be normalized so that the transformation is canonical and the c’s obey the same commutation relations as the a’s, e.g.,



and can see LHS = δEE´ only if the ψ are normalized.

*Another way*

Might recall that the operator which creates/destroys exact excitations of H will follow,



which is kind of an ‘eigenvalue equation’ for the operators. This is true regardless of whether we have interactions or not. Well let’s suppose



(in other cases, more general suppositions are possible) and try to work out what the coefficients would be:



Now we’re dealing with fermions so we don’t know the commutators, but can still proceed,



So we need,



The independent operators aj are the independent d.o.f., so have to separate out all of them alone. So can write this as:



So we must have:



Taking complex conjugate of both sides, and using Hermiticity of V (so that Vjk\* = Vkj) we have:



which is the same as above.

*And another way*

Another way is the equation of motion way. Consider the equation of motion of ak. Luckily we already did most of the work.



So our equation is:



which is just what we said it’d be up above. This is a matrix equation involving all the ak’s, which if we solve, we’ll get the energies. Not going to keep going. But this is the approach taken when we look at Green’s Functions. It can be streamlined pretty well, and generalizes well to when we have interactions.

**Example**

As an illustrative case, consider N sites arranged in a ring. We’ll say the sites are separated by distance ‘d’, and that the ring has length L = Nd. Might see tight binding model for helpful context. We can think of each site as having a singly ionized atom placed there, and we’re looking at the ionized electrons moving in the potential field of these atoms. So each site has a bare energy ε which includes the kinetic and potential energy of the electron under the influence of that site’s atom. And can say that the electron feels the potential due to neighboring sites as well. And so we can write a prospective Hamiltonian as:



where ajσ annihilates electron with spin σ (up or down) on site j. Being on a ring, we will impose periodic boundary conditions so that ai=0,σ = ai=N,σ. This guy is often used to model electrons in a periodic crystal. Anyway. So we want the energy levels. Let’s do the commutator thing. So we’ll look for the exact annihilation operator, which satisfies:



And let’s suppose it’s a linear combination of the a’s.



Then feeding this in (could just use equation above, but…)



Working out that commutator,



Now filling into our equation,



Now get the akσ’s all together. Will change variable of summation k → k – 1 in second sum, and k → k + 1 in third sum,



And taking complex conjugate, noting V is a real number, we have our eigenvalue equation.



Now this is a *difference* equation. Solutions to these are similar to those of differential equations. We’ll make an ansatz ψk = Aeλk (might note that if ε were site-dependent, i.e., depended on k, then this ansatz wouldn’t work – we need constant coefficients just as in ODE) Then,



But can λ be anything? We have those periodic boundary conditions on the ak’s which is equivalent to such a condition on the ψk’s.



(n can only range over N total values as can verify that when let n go past this, we just end up repeating ourselves, i.e., ψ(n + N)k = ψ(n)k) What about A? That should normalize our eigenvector. We need,



We’ll just say A = 1/√N. So then we have ψj(n) = (1/√N)e-λ\_n·j, and so:



cnσ is the excitation annihilation operator. And cnσ† would create excitations. All the excited states would just be N applications of cnσ†, with different n’s, onto the particle vacuum |0>. And En is the energy spectrum. A general excited state, and its energy, would be:



It’s more standard to write this as:



and,



where k is a wavevector that ranges over the values [0, 2π·1/Nd, 2π·2/Nd, …, 2π·(N-1)/Nd]. Actually, it is more standard to shift the range of n from [0, 1, 2, .., N-1], to [-N/2, -N/2+1, -N/2+2, …, N/2-1], in which case k’s range shifts to [-π/d, -π/d + 2π·1/Nd, -π/d + 2π·2/Nd, …, π/d-2π·1/Nd], often just written as [-π/d, π/d). And R is the position vector of the jth site and ranges over values [0, d, 2d, 3d, …, (N-1)d] = [0, d, 2d, .., L – d], which we could write as [0, L). Anyway, so we’ve found the energy levels. The N-fold degeneracy of ε energy levels has been lifted. And if we want, we can put the Hamiltonian in terms of our new eigenstate-operators. First have to solve for aRσ in terms of them,



So we have:



And filling this into our H,



we have:



which is of course,



which clearly evinces that ckσ is our excitation annihilation operator. Energy band looks something like this:

A diagram of a function

Description automatically generated

The width of the band is proportional to V.

**Example**

If we add two-particle interactions, then it gets tough. One usually doesn’t resort to perturbation theory (but could…), but rather approximation schemes using Variational Principle, or Green’s Functions. But let’s go ahead and try it. So looking ahead to the tight-binding model, a common approximate incorporation of the Coulomb interaction between electrons is this model:



where nR↑ = cR↑†cR↑ is the spin up occupation number for site j, and similarly for the spin down guy. So basically, we only consider Coulomb interactions on-site. Filling in the number operators,



Unfortunately, we cannot solve this one exactly. But we can use perturbation theory. Let’s try simple first order perturbation theory. Well, before we do, let’s put everything in the single particle H eigenbasis,



Then,



One way to satisfy the constraint is to write it like this:



So that’s simpler. And now we’d just import our formulas for the eigenstates and energies from perturbation theory.



Well let’s consider the ground state. |ψGS> is the lowest energy state ket. Without the interaction, it would just be the set of N electrons filled from k = 0 to k = ±kF, a state often designated as |ψGS(0)> = |F>. This has an unperturbed energy EGS(0) = Σ|k|<kF(Ek), whatever that is. If can use parabolic approximation to the energy spectrum, then this would be EGS(0) = NEF/3 (assuming 1D anyway, and why am I assuming 1D?), where EF = kF2/2m\* (see Condensed Matter/Metals/Free Day/Electrons/Excitations/Properties file). The filling is depicted below.

A diagram of a function

Description automatically generated

With the interaction turned on, the state and energy should change. What is the energy? Well to first order, the new ground state energy would be:



Now let’s try to work this out,



From the latter expression it is clear that to have non-zero overlap, we must have k = k + q, ad k´ = k´-q. So q = 0. Also, in order for the operators to not annihilate our state, we need k+q < kF → k < kF and k´ - q < kF → k´ < kF. If these conditions are met, then the overlap is 1. So we have:



Each of the sums gives N/2 (instead of N because we’re not summing over spins too). So,



Can we interpret this? I guess I’d say, we have N electrons and 2N spots to we can fill. I’d say there is a 50-50 change of a given orbital being occupied, which would correspond to an expectation of (0.5)(2N) = N particles, as it should. And so then there is a (1/2)(1/2) = ¼ chance that a given orbital is doubly occupied. Then energy associated with that would be V0. So the energy expectation is (1/4)NV0. We could try to work out the new ground state to first order. We’d have:



where {k} means the set of N k values between [-π/d, π/d), subject to the restriction that each k can be repeated no more than twice (Pauli-Exclusion principle). And this is:



In order for the overlap to be non-zero, we must have:



For |ψGS(0)> not to be annihilated by these operators, we need, due to the Pauli-exclusion principle,



Ugh. I have no desire to simplify this. And the energy denominator would come to:



So our PT formula comes to:



where we recall |ψ{k}(0)> must be given by (all those c’s)|ψGS(0)>, in order for the overlap to be 1. This is pretty messy, and illustrates why calculating wavefunctions is not something we want to be doing in many-body problems. The Green’s Functions approach is much more tractable. But before we go, let’s return to H,



And let’s look at the opposite limit, where V0 is super large, and Ek small by comparison. In this limit, we’ll want to stay in position space, rather than Fourier space, as the Coulomb interaction term is already diagonal in position space. The eigenstates are just the position space occupation numbers. And the energy is just V0 × the number of doubly occupied orbitals. So, repeating myself.



Here’s a couple states,

A group of arrows pointing to the top

Description automatically generated with medium confidence

The unperturbed GS would be where we have no doubly occupied orbitals – all orbitals are singly occupied. And the energy would be 0.



The first excited state(s) would be all states with just one doubly occupied orbital, and the energy would be V0. And similarly the second excited state(s) would be constructed.

We’ll observe the GS is 2N-fold degenerate, because we can point our spins in any direction. We’d like to see how the addition of the orbital and hopping terms lifts this degeneracy. So according to PT, we need to diagonalize the perturbation within the subspace of our degenerate GS.



The perturbation is the blue stuff, and, well, turns out the perturbation already is diagonal, because the εaRσ†aRσ term is diagonal in that subspace. And the V(aRσ†aR+d,σ + aR+d,σ†aRσ) term is zero. So we go to 2nd order PT,



And focusing on the GS, or rather, one of the GS’s.



Let’s say we’re interested in this result, to first order in V/V0. Then we need only concern ourselves with Ei(0) which are first excited states. And then EGS(0) – Ei(0) = -V0. So can say,



The blue operator takes a spin at R and moves it to R+d, or takes a spin at R+d and moves it to R, unless the Pauli Exclusion principle forbids it, in which case we just get zero. So in fact, it creates 1st excited states. If we think about it, we can see that a |ψGS(0)> with all spins up or all spins down will just return zero when operator on by the blue guy. And in fact the |ψGS(0)> with alternating spins will always return something non-zero when acted on by the blue operator. And so, thanks to the minus sign, it will be the lowest energy state. So let’s focus on *that*.



Looks like with N sites, there are about 2N first excited states that one can create by moving a spin into an adjacent site to the right, or to the left, like this:



and for every excited state, the blue operator acting on the GS,



should eventually generate it. As we can And when it does,



will give us 1. Otherwise 0. So ultimately, we should get:



So,



And FWIW, we can see that the GS would be anti-ferromagnetic so-to-speak, since the spins are all anti-aligned.